

Synergistic Effect of Cinnamon (*Cinnamomum burmannii*) Leaves Extract and Potassium Iodide on Mild Steel in HCl

Rohil¹, Yeni Stiadi², Emriadi^{3*}

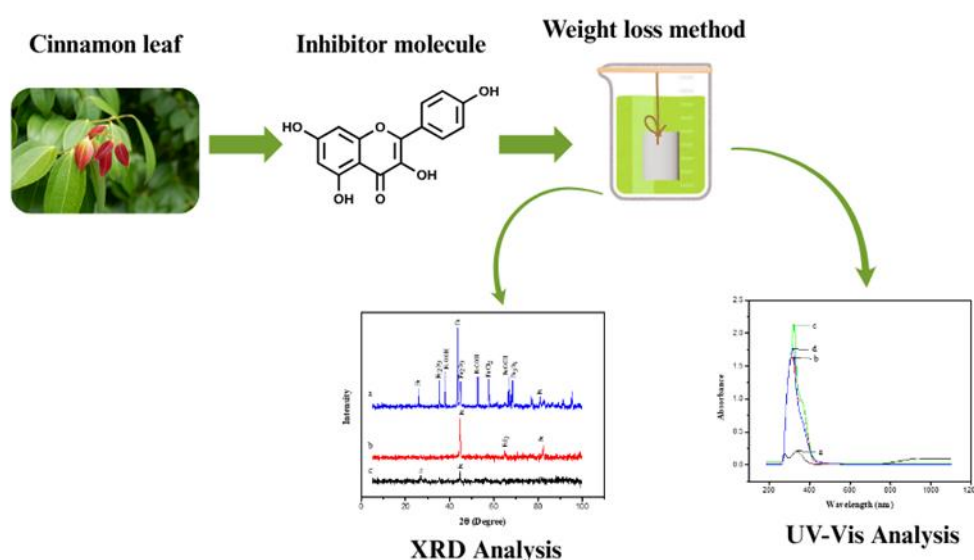
^{1,2,3}Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang, 25163, Indonesia

Abstract

The synergistic impact of potassium iodide with cinnamon leaf extract (CLE) on hindering gentle steel corrosion in a HCl arrangement was examined utilizing weight loss measurement, UV-Vis spectroscopy, and X-ray diffraction (XRD) analysis. At an inhibitor concentration of 10 g/L CLE coupled with 0.04 g/L potassium iodide, the inhibition efficiency increased from 92.8% to 97.06% as the temperature and concentration increased. The Langmuir adsorption isotherm was followed by the inhibitor's adsorption on the mild steel surface. The synergistic interaction between CLE and potassium iodide was validated when the synergistic parameter (S) was greater than 1. The inhibitor components and the steel surface formed a coordination complex, according to UV-Vis analysis. When CLE was present, a defensive layer formed on the mild steel surface that prevented the corrosive medium from interacting with the metal, as confirmed by XRD analysis. These results imply that potassium iodide and CLE may be useful and sustainable corrosion inhibitors for mild steel in acidic environments.

Keywords: Mild Steel; corrosion inhibitor; cinnamon; weight loss; synergistic effect

Graphical Abstract



* Corresponding author
Email addresses: emriadi@sci.unand.ac.id

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Introduction

Mild steel is commonly utilized in mechanical applications because of its excellent mechanical properties and cost-effective production. Nonetheless, mild steel is particularly prone to corrosion, especially when exposed to acidic environments like HCl solutions commonly used in metal cleaning and processing industries [1]. Therefore, preventive measures must be taken to reduce rust. Here are some other materials that can be used as anti-rust agents, such as *Gleichenia linearis* burm. leaf extract [2] and *Melastoma candidum* D. leaf extract [3]. The presence of hetero atoms like sulfuric, oxygen, or nitrogen in relevant molecules, along with heterocyclic compounds and π -electrons, influences the effectiveness of inhibitors. These chemical inhibitors can adhere to the metal surface and obstruct active sites, which in turn lowers the corrosion rate [4]. One example of an effective natural inhibitor is cinnamon leaves.

Cinnamon is a perennial plant that takes a long time to yield results. The bark of the branches and trunk steel is the main product of the cinnamon plant, while the twigs and leaves are by-products [5]. The bark of cinnamon is widely utilized by the community, whereas the leaves have not been optimally utilized. Cinnamon leaves are rich in various compounds, including flavonoids, alkaloids, saponins, tannins, phenolics, and hydroquinone [6]. These compounds have demonstrated the ability to inhibit corrosion, as evidenced by previous studies of *Mikania micrantha* extract [7] and *Cardaria draba* extract [8]. The synergistic effect for halides is ordered as follows: $I^- > Br^- > F^- > Cl^-$. Combining iodide with organic inhibitors can improve the effectiveness of corrosion inhibition for mild steel in harsh conditions, as iodide ions offer benefits like larger atomic size and easier polarization [9]. This study aims to see how effective small amounts of potassium iodide and CLE are at preventing corrosion on mild steel, as well as their synergistic effects that provide valuable insights into strategies for inhibiting corrosion of mild steel in acidic environments.

This research focuses on the synergistic effects of potassium iodide and CLE in HCl media, aiming to develop practical methods for corrosion inhibition in mild steel applications. This study on

mild steel seeks to explore the combined effects of CLE and iodide inhibitors on steel corrosion in acidic solutions, employing weight loss methods, XRD analysis, and UV-Vis spectroscopy.

Materials and Methods

Materials

Cinnamon leaf samples, mild steel (AISI 1020), hydrochloric acid (Smart Lab) p.a, potassium iodide (EMILD STEELURE® ACS, ISO, Reag. Ph Eur), deionized water (H₂O), methanol (CH₃OH) p.a, and acetone.

Preparation and Extraction

Preparation of cinnamon leaf and the making of CLE. Fresh cinnamon leaves are taken in Koto Tuo Pulau Tengah, Kerinci, Jambi, as much as 5 kg, chopped into pieces and dried at room temperature until dry, then weighed to obtain dry powder. 500 g of dried cinnamon leaf powder is drenched in 3000 mL of methanol p.a for 3 days, at that point sifted. The extract gotten is vanished employing a revolving evaporator (*HEIDOLPH w200*).

Weight Loss Method

The corrosion rate was decided utilizing weight loss method, considering the influence of temperature, by immersing steel in 50 mL of 1 M HCl medium solution with various concentrations of CLE and addition of potassium iodide with temperature variation (30, 40, 50, and 60°C). Steel was soaked using a water bath for 7 hr. Then cleaned, cleaned and dried using an oven. After drying, the steel is weighed and the weighing result was communicated as the ultimate weight (m_2). The corrosion rate was calculated according to equation 1.

$$V_{\text{corr}} = \frac{m_1 - m_2}{A \cdot t} \quad (1)$$

Where m_1 and m_2 are the sample weights prior to and following immersion in the corrosive solution, and V_{corr} stands for the corrosion rate. Respectively, A denotes the exposed area, and t is the immersion time in hours. The inhibitor efficiency (IE%) was determined according to equation 2.

$$EI(\%) = \frac{V_{\text{corr}(\text{blank})} - V_{\text{corr}(\text{inh})}}{V_{\text{corr}(\text{blank})}} \times 100\% \quad (2)$$

Where $V_{\text{corr}(\text{blank})}$ and $V_{\text{corr}(\text{inh})}$ represent the corrosion rate without and with the inhibitor in the HCl solution, respectively.

Spectroscopy UV-Vis Analysis

The steel was submerged in a 1 M HCl corrosive liquid in order to perform UV-Vis spectrophotometric measurement with or without 10 g/L CLE and 0.4 g/L potassium iodide, for 7 days. After soaking in the solution, it was then taken and measured at wavelengths between 200 and 800 nm using a UV-Vis spectrophotometer. This measurement was also carried out for 1 M HCl only by soaking without adding CLE. The purpose of these measurements is to see how the inhibitor components (CLE and potassium iodide) form coordination complexes with the steel surface.

X-Ray Diffraction (XRD) Analysis

XRD measurements were conducted by immersing the mild steel in a 1 M HCl corrosive medium, both without and with the addition of

10 g/L CLE for 7 days, as well as with the addition of 0.4 g/L potassium iodide. After soaking, the steel was dried, and the adhered layer was scraped off the surface. This measurement aims to confirm the nearness of a defensive layer formed by CLE on the steel surface, which makes a difference avoid the destructive medium from association with the metal.

Result and Discussion

Analysis Using Weight Loss Method

Weight loss data for different CLE concentrations at various temperatures can be utilized to determine the corrosion rate and inhibition efficiency values. Figures 1 and 2 show that the corrosion rate decreases as the CLE concentration increases. However, with the addition of potassium iodide, the corrosion rate increases with rising temperature during the 7 hours immersion period. This decrease in corrosion rate indicates that CLE is effective in inhibiting corrosion in an HCl acid medium. This inhibitory effect occurs because the CLE extract adheres to the steel surface [10].

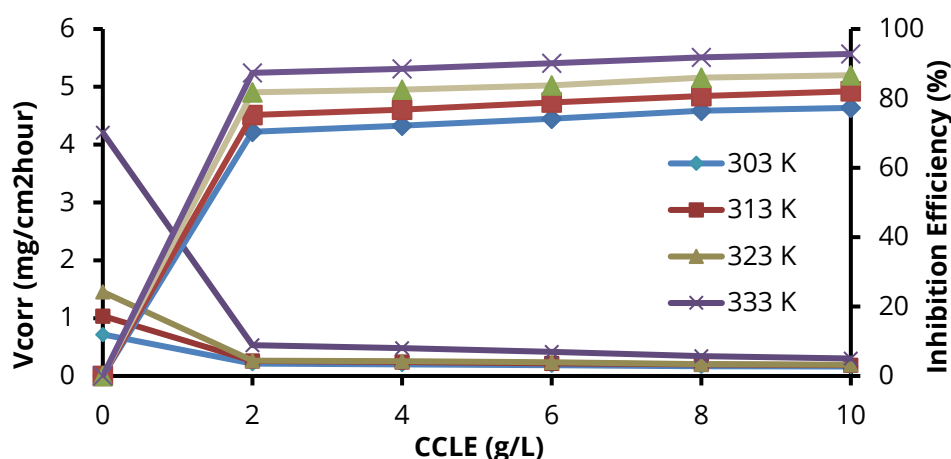


Figure 1. Effect of CLE concentration on inhibition efficiency (%) and corrosion rate (V_{corr}) in 1 M HCl at diverse temperatures.

Figures 1 and 2 show that the higher the concentration, the higher the efficiency. and the higher temperature, the higher the efficiency. The addition of iodide synergistically increases an inhibition efficiency with an addition of 10 g/L of CLE as an inhibitor, the inhibition efficiency

reaches 92.8% at a temperature of 60°C, adding 0.04 g/L of iodide boosts the inhibition efficiency to 97.06%. Higher iodide concentrations lead to more molecules being adsorbed onto the metal surface [11,12].

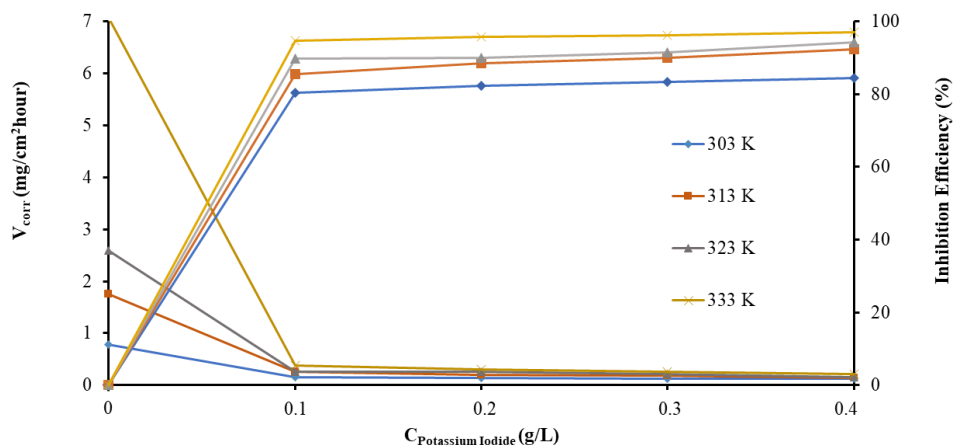


Figure 2. Effect of CLE and potassium iodide concentration on inhibition efficiency (%) and corrosion rate (V_{corr}) in 1 M HCl at different temperatures.

Adsorption Isotherm

Adsorption isotherm mild steel explains how the inhibitor engages with the carbon steel surface. Among the various adsorption isotherm models examined, counting Temkin, Freundlich, and Langmuir, the Langmuir model seems to be the most suitable which can be seen in Table 1. Because, the coefficient of determination (R^2) values approaching 1 clearly demonstrate this.

The Langmuir isotherm condition as illustrated in equation 3.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{3}$$

where K_{ads} advertisements speaks to The harmony consistent for the adsorption prepare, where C speaks to the inhibitor concentration and θ demonstrates the surface scope [2,13].

Table 1. Determination coefficient (R^2) values for different adsorption isotherms.

Temperature (K)	Coefficient of determination (R^2)		
	Langmuir	Freundlich	Temkin
303	0.9997	0.9975	0.9970
313	0.9992	0.9998	0.9713
323	0.9992	0.9996	0.7301
333	0.9999	0.9999	0.9710

Figure 3. Exhibits a linear correlation between C/θ and C in the 303–333 K temperature range. As seen by Table 1, this linear relationship implies that the adsorption of inhibitor compounds is more consistent with the Langmuir adsorption model than with alternative isotherm models. The Langmuir adsorption isotherm is employed because the coefficient of determination (R^2) is near 1. This shows that the molecules stick to the mild steel surface in a single layer, implying that the produced layer is a single layer (monolayer). Moreover, the connection between the CLE and

potassium iodide compounds and the mild steel is stronger [14].

The K_{ads} value is derived from the captured of the linear condition delineated in Figure 3. The adsorption strength of potassium iodide and CLE on the mild steel surface is indicated by this number. The calculation of ΔG_{ads} can be derived from the K_{ads} constants, which were observed according to the formulation described in equation 4.

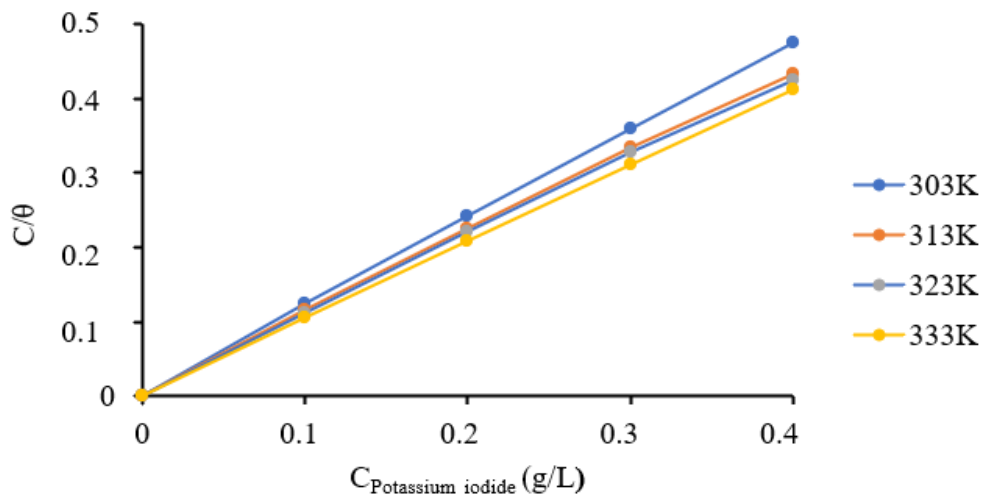


Figure 3. The inhibitor is Langmuir adsorption graphs at various temperatures on a mild steel surface in a 1 M HCl solution.

$$\Delta G_{ads} = RT \ln (C_{H_2O} K_{ads}) \tag{4}$$

Where, R is the molar gas constant (8.314 J mol⁻¹K⁻¹) C_{H₂O} is the water content (1000 g/L), and. A negative ΔG_{ads} value between from -20 to -40 kJ/mol indicates that both physisorption and chemisorption processes are involved in are involved in the spontaneous adsorption process. During the adsorption process at the solid-liquid interface, molecules of the solute and solvent can both stick to the CLE surface [15]. The value of ΔG_{ads} can be used to determine the enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption, as calculated using equation 5.

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T} \tag{5}$$

In this context, ΔH_{ads} represents the enthalpy of adsorption (kJ/mol), ΔG_{ads} represents the Gibbs free energy (kJ/mol), ΔS_{ads} indicates the entropy of adsorption (J/mol), and T stands for the temperature (K). Table 2. Show that the ΔH_{ads} which is probably why the adsorption entropy has a positive sign. The adsorption process is characterized by its endothermic nature indicates the dominance of chemical adsorption. The positive ΔS_{ads} value indicates a decrease in disorder. When the inhibitor adsorbs onto the steel surface in an acidic solution, the number of adsorbed inhibitor molecules increases relative to the number of water molecules that leave the surface [8,16,17].

Table 2. The Langmuir isotherm is used to calculate the thermodynamic parameters for the adsorption of CLE on mild steel in a 1 M HCl setup at various temperatures.

Temperature(K)	K _{ads}	ΔG ^o _{ads} (kJ/mol)	ΔH ^o _{ads} (kJ/mol)	ΔS ^o _{ads} (J/mol.K)
303	284.284	-31.632		
313	185.410	-31.564	21.966	174.010
323	241.558	-33.283		
333	627.963	-36.958		

Thermodynamic Parameters Activation

The Arrhenius condition (equation 6) can be utilized to decide the activation energy by

plotting the relationship between 1/T and ln V_{corr} of steel at various temperatures.

$$\ln V_{corr} = \ln A - \frac{E_a}{RT} \tag{6}$$

Where A speaks to the recurrence figure, E_a denotes the activation energy (kJ mol^{-1}), and T stands for temperature (K).

In Figure 4, the natural logarithm of the corrosion rate ($\ln(\text{CR}/T)$) is plotted against the inverse of the absolute temperature ($1/T$). The slopes of the Arrhenius and transition state conditions can be used to determine the activation energy (E_a) and activation enthalpy (ΔH_{ads}). The findings pertaining to metal corrosion mechanisms in

acidic conditions that are suppressed and those that are not are shown in Table 3. In the absence of CLE and with potassium iodide present, the activation energy is greater than that observed in the inhibited solution. As temperatures rise, the amount of surface area occupied by CLE increases, and the presence of potassium iodide may lead to an imprecise reduction in E_a , modifying the erosion energy by advertising elective chemical pathways that have lower enactment energies⁸.

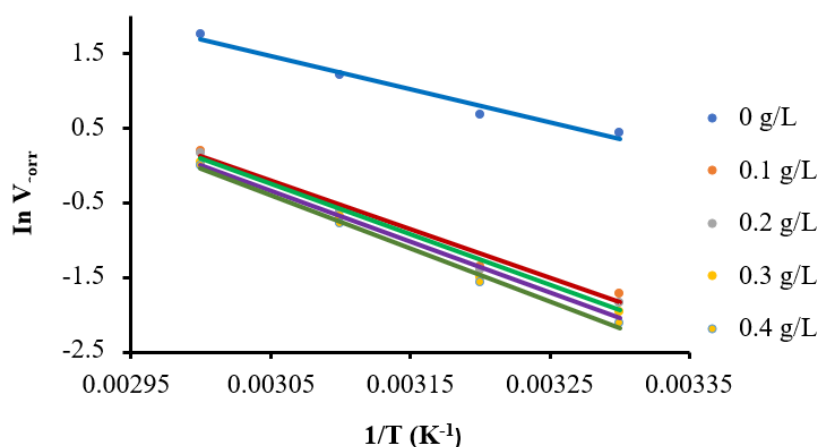


Figure 4. Charts of Arrhenius plots outlining the disintegration rates of mild steel in a 1 M HCl arrangement, both within the nonappearance and nearness of CLE with potassium iodide at distinctive concentrations.

To find the values of ΔH^* and ΔS^* , the Arrhenius condition can be utilized (7).

$$\ln \frac{V_{\text{corr}}}{T} = \left[\ln \left(\frac{R}{Nh} \right) + \frac{\Delta S^*}{R} \right] - \frac{\Delta H^*}{RT} \quad (7)$$

Where N is Avogadro's number (6.023×10^{23}), h is Planck's constant (6.63×10^{-34}), ΔS^* represents the variation in entropy ($\text{J mol}^{-1} \text{K}^{-1}$), and ΔH^* denotes the enthalpy variation ($\text{J mol}^{-1} \text{K}^{-1}$).¹⁸⁻¹⁹ Table 3. show that the positive ΔH^* esteem shows that the method was an

endothermic response. This recommends that the erosion prepare requests a significant sum of energy³. Meanwhile, the ΔS^* values watched both with and without the tested extract were found to be negative, demonstrating that the rate-determining step including the actuated complex is characterized by affiliation instead of separation. This suggests that the activated molecules exist in a more disordered state relative to their initial condition⁴¹¹.

Table 3. Values for activation energy (E_a), activation enthalpy (ΔH^*), and activation entropy (ΔS^*).

Potassium Iodide concentration (g/L)	Activation Energy (E_a) (kJ/mol)	Activation Enthalpy (ΔH^*) (kJ/mol)	Activation Entropy (ΔS^*) (J/mol.K)
0	55.481	55.481	-63.956
0.1	19.851	19.851	-194.448
0.2	18.816	18.816	-198.855
0.3	17.024	17.024	-205.520
0.4	11.362	11.362	-225.399

Synergistic Effect. With adding potassium iodide results in increased inhibition efficiency increases compared to using CLE by itself. The equation below is used to determine the synergistic effect, as shown in equation 8 [14].

$$S_1 = \frac{1 - \theta_{1+2}}{1 - \theta_{1+2}} \quad (8)$$

Where, S represent synergism. θ_1 indicates the amount of surface coverage by iodide ions, θ_2 denotes the level of coverage on the surface by CLE, and θ_{1+2} reflects the total surface scope combining iodide ions and CLE. A synergistic effect value (S) exceeding 1 signifies a synergistic interaction between CLE and potassium iodide, as can be seen in Table 4. This suggests that the combination of CLE with potassium iodide is more efficient in inhibiting corrosion compared to when used separately [16,20]. An S value greater than 1 signifies a synergistic relationship, whereas an S value less than 1 signifies an antagonistic relationship and an S value = 1 indicates no synergistic or antagonistic relationship between the compounds [4,21].

Table 4. Synergistic effect values of MLE combined with potassium iodide at 60°C

Potassium iodide Concentration (g/L)	Synergistic Effect (S)
0	-
0.1	1.553
0.2	1.550
0.3	1.424
0.4	1.420

UV-Vis Analysis

UV-Vis analysis was conducted on mild steel to determine the interaction of the inhibitor complex with the steel surface. As shown in Figure 5, the UV-Vis spectrum of the HCl solution with steel (Figure 5a) exhibits a peak at 337 nm. In contrast, the spectrum of the HCl solution with CLE extract (Figure 5b) shows an absorption peak at 314 nm. Meanwhile, the mixture of CLE extract and steel (Figure 5c) displays a peak at 322 nm.

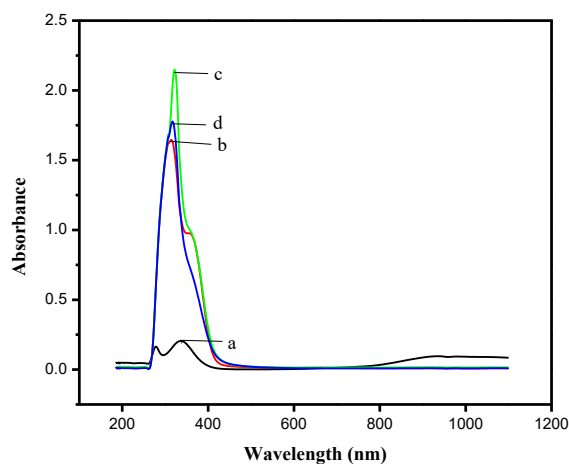


Figure 5. UV-Vis Spectra (a) 1 M HCl + mild steel, (b) 1 M HCl + CLE 10 g/L, (c) 1 M HCl + CLE 10 g/L + mild steel, and (d) 1 M HCl + CLE 10 g/L + potassium iodide 0,4 g/L + mild steel.

This absorption peak is associated with an $n \rightarrow \pi^*$ electronic transition of the C=O group present in the CLE extract [22]. Additionally, the UV-Vis range of the CLE extract arrangement with steel and the expansion of potassium iodide (d) appears a top at 317 nm. This top move demonstrates the creation of a coordination complex including the components of the CLE extract with steel all through the dousing handle [14]. XRD Analysis. X-Ray Diffraction (XRD) the investigation was conducted on mild steel to decide the compounds show within the detached

layer shaped on its surface. Figure 6 (a) shows several peaks indicating the presence of iron oxides, namely Fe_2O_3 and Fe_3O_4 . Additionally, $FeCl_2$ is also present, shaped as a result of the interaction of chloride particles with the substrate [23]. Figure 6 (c) shows no intensity peaks of $FeCl_2$, indicating that CLE can reduce the corrosion process by forming a protective layer on the steel surface and preventing the corrosive medium HCl from interacting with the mild steel surface. Figure 6 (b) shows a small amount of iron oxide and the appearance of Fe_2 peaks.

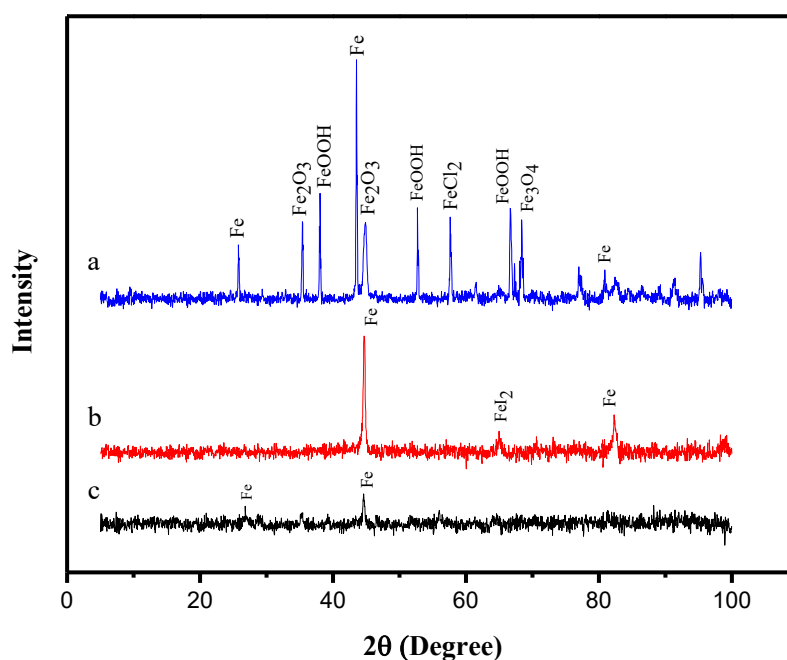


Figure 6. XRD designs (a) mild steel submerged in 1 M HCl, (b) mild steel submerged in 1 M HCl + CLE 10 g/L + potassium iodide 0.4 g/L, and (c) mild steel submerged in 1 M HCl + CLE 10 g/L.

Conclusions

Cinnamon leaf remove and potassium iodide mix act has been showed up to be a practical disintegration inhibitor for delicate steel in a 1 M HCl course of action. An increment in temperature and the incorporation of iodide leads to progressed restraint productivity due to a result of synergistic impact. The Langmuir adsorption isotherm is used to alter the CLE is adsorption behavior. The synergistic parameter (S), analyzed at different iodide concentrations. The esteem was decided to surpass one, recommending that the improved hindrance effectiveness watched with iodide particles is due to their synergistic interaction.

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Author Contributions

R: collecting primary data, processing raw data and writing-original draft. Y.S: Supervision, research design, data analysis, and data interpretation, and validation. E: Funding

acquisition, critically reviewed, writing initial draft, data analysis, editing, and revising.

Conflict of interest

The authors declare no conflict of interest.

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